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Dynamics of liquid N_2 at $T = 66.4$ K studied by neutron inelastic scattering

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Neutron inelastic scattering from liquid N_2 at $T = 66.4$ K and saturated vapor pressure is presented in the form of the normalized coherent nuclear-scattering law $S_{n,\mathrm{coh}}(\kappa,\omega)$. Our results at the wave vector, $\kappa = 0.1$ Å^{-1} are consistent with recent computer simulation showing that the sound mode continues to propagate for larger wave vectors than described by linear hydrodynamic theory. At larger wave vectors no evidence is found of propagating phononlike excitations in this liquid, but the observed spectra are broad and centered around the mean recoil energy of a Boltzmann gas. Using Sears' partial-wave expansion to separate the scattering owing to rotational motion from that owing to the motion of the molecular centers, we compare the latter to the result obtained from liquid argon, appropriately scaled according to the principle of corresponding states. The over-all agreement is good, but significant deviations from scaling are observed and briefly discussed in terms of anisotropic interactions. Further, the information obtained on rotational relaxation is compared with recent experiments and theories.

I. INTRODUCTION

During recent years considerable interest has been devoted to the dynamics of monatomic liquids.[1] Except for the motion of protons in hydrogenous liquids, however, only in a few cases have more complicated systems been studied outside the long-wavelength regime. However, very recently considerable interest has been devoted to the condensed phases of molecular nitrogen. Both neutron diffraction[2] and computer simulation[3] on this liquid have been performed and further work is in progress. Also, NMR[4] (nuclear-magnetic-resonance) and Raman[5] scattering experiments have been done. Further, the dynamics of the solid phase have been investigated by neutron scattering.[6]

In this paper we present neutron inelastic scattering from liquid nitrogen at the temperature $T = 66.4$ K and saturated vapor pressure. Our reason for studying this system is in part that the extensive experimental evidence obtained from monatomic liquids justifies the study of more complicated ones, and that N_2 may here be taken as a simple example. Of importance is the fact that nitrogen has good neutron-scattering properties and that neutron scattering from a homonuclear molecular liquid may be unambiguously interpreted, since only one scattering length is involved. Also, two particularly interesting problems could be studied in liquid N_2, namely, the existence of propagating modes at small wave vectors, and the extent to which the motion of molecular centers is influenced by molecular anisotropy.

In Sec. II we present and discuss the theory for interpreting the neutron-scattering data. Section III describes the experimental details, and in Sec. IV we give the corrected and normalized results. These are discussed in context with the proposed theories in Sec. V. Our main conclusions are then summarized in Sec. VI.

II. THEORY OF NEUTRON SCATTERING FROM MOLECULAR NITROGEN

The neutron scattering from a system of N_n nuclei is conveniently described by the double differential cross section,[7]

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{N_n}{4\pi}\frac{k}{k_0}\left[\sigma_{\mathrm{coh}} S_{n,\mathrm{coh}}(\kappa,\omega) + \sigma_{\mathrm{inc}} S_{n,\mathrm{inc}}(\kappa,\omega)\right]. \tag{1}$$

In (1) $\vec{k}_0$ and $\vec{k}$ are the incoming and outgoing wave vectors for the neutrons; $\kappa = \vec{k}_0 - \vec{k}$ and $\hbar\omega = (k_0^2 - k^2)/2m_n$ are the respective wave vector and energy transferred to the system from a neutron; σ_{coh} and σ_{inc} are the coherent and incoherent neutron-scattering cross sections. The two scattering laws $S_{n,\mathrm{coh}}$ and $S_{n,\mathrm{inc}}$ are the Fourier transforms of the total and self-van Hove-correlation functions for the nuclei. Because of the principle of detailed balance, the scattering laws obey the relations

$$S_{n,\mathrm{coh;inc}}(\kappa,\omega) = e^{\hbar\omega/k_B T} S_{n,\mathrm{coh;inc}}(\kappa,-\omega). \tag{2}$$

Further, the following sum rules state that

$$\int_{-\infty}^{\infty} S_{n,\mathrm{coh}}(\kappa,\omega)\,d\omega = S_n(\kappa), \tag{3a}$$

$$\int_{-\infty}^{\infty} S_{n,\mathrm{inc}}(\kappa,\omega)\,d\omega = 1, \tag{3b}$$

where $S_n(\kappa)$ is the nuclear structure factor.

Since any classical calculation, either analytic or a computer simulation, yields a symmetric scattering law, Schofield[8] proposed that (2) be used to define a "symmetrized scattering law,"

$$\tilde{S}(\kappa,\omega) = e^{-\hbar\omega/2k_BT}S(\kappa,\omega), \tag{4}$$

which could be used to relate an observed scattering law to the result of such calculations. The use of $\tilde{S}(\kappa,\omega)$ is equivalent to applying a first-order quantum correction to the classical calculation, and this has been proven quite useful in the study of almost-classical liquids.

Whereas exact values for the frequency moments have been calculated by deGennes for monatomic systems,[9] this has not been done for the molecular case, owing to the correlations arising from the internal modes of molecules. The moment relations consequently cannot be used to check the measured spectra, and we cannot in the present work compare our data to the approximate theoretical moment relations obtained for the diatomic case.[9] This is in part owing to our lack of treatment of multiple scattering.

As pointed out by Sköld *et al.*,[10] one main problem in obtaining the normalized scattering laws is multiple scattering. Since (1) holds for singly scattered neutrons, the multiply scattered neutrons must be subtracted from the spectra before the scattering laws can be analyzed. A satisfactory treatment of this effect through the Monte Carlo program MSCAT[11] requires a model input for the correct scattering laws, but we have not been able to use this attractive approach in the absence of an appropriate model for N_2. Hence we are in the present case unable to correct for multiple scattering, but using the experience from Ref. 10, we believe that we can avoid misinterpretation of the data due to this effect. In Ref. 10 it was found that the multiple scattering spectra were rather broad in energy compared with the primary spectra, and therefore multiple scattering makes serious contributions to the higher moments of $S(\kappa,\omega)$. Since we here concentrate on the lower-energy part of the spectra, and only use the "zeroth" moment (3), we believe that our lack of multiple scattering treatment does not influence our conclusions substantially.

Sears[12] has worked out an alternative expression for the cross section (1) of N diatomic homonuclear molecules in the weakly hindered rotational approximation, considering the translational and rotational motion separately:

$$\frac{d^2\sigma}{d\Omega\,d\omega} = 2N\frac{k}{k_0}\,e^{\hbar\omega/2k_BT}\frac{\sigma_{\mathrm{coh}}}{4\pi}\times\left[a_{\mathrm{coh}}(\kappa)\tilde{S}_{\mathrm{coh}}(\kappa,\omega) + a_{\mathrm{inc}}(\kappa)\tilde{S}_{\mathrm{inc}}(\kappa,\omega)\right] + \sum_{l=1}^{\infty}\left(a_l(\kappa)\int_{-\infty}^{\infty}\tilde{S}_{\mathrm{inc}}(\omega-\omega')S_l(\omega')\,d\omega'\right). \tag{5}$$

Because liquid N_2 may be considered to be almost classical, $\tilde{S}_{\mathrm{coh}}(\kappa,\omega)$ and $\tilde{S}_{\mathrm{inc}}(\kappa,\omega)$ in (5) present the symmetrized scattering laws for the molecular centers. Not yet defined in (5) is the rotational scattering law $S_l(\omega)$, which is the Fourier transform of the lth rotational relaxation function $F_l(t)$:

$$S_l(\omega) = (1/\pi)\int_0^{\infty} F_l(t)\cos(\omega t)\,dt. \tag{6}$$

The form factors for each of the scattering laws in (5) are the following:

$$\begin{aligned} a_{\mathrm{coh}}(\kappa) &= 2j_0^2(\tfrac{1}{2}\kappa d), \quad a_{\mathrm{inc}}(\kappa) = \frac{\sigma_{\mathrm{inc}}}{\sigma_{\mathrm{coh}}}\,j_0^2(\tfrac{1}{2}\kappa d),\\ a_l(\kappa) &= (2l+1)j_l^2(\tfrac{1}{2}\kappa d)\left(2+\frac{\sigma_{\mathrm{inc}}}{\sigma_{\mathrm{coh}}}\right), \quad l \text{ even}\\ &= (2l+1)j_l^2(\tfrac{1}{2}\kappa d)\frac{\sigma_{\mathrm{inc}}}{\sigma_{\mathrm{coh}}}, \quad l \text{ odd.} \end{aligned} \tag{7}$$

In (5) and (7) j_l is the lth spherical Bessel function and $d = 1.094$ Å is the bond length for the N_2 molecule.

The main difficulty in calculating a_{inc} and the a_l's lies in the uncertainty of σ_{inc}, for which no accurate value has been published. From Willis[13] one can estimate $\sigma_{\mathrm{inc}}/\sigma_{\mathrm{coh}} \sim 0.03$, but from the discussion in Sec. V B it is natural to assume either $\sigma_{\mathrm{inc}}/\sigma_{\mathrm{coh}} \approx 0$ or $\sigma_{\mathrm{inc}}/\sigma_{\mathrm{coh}} = 0.03$. Consequently, in interpreting the spectra, the two possibilities must be considered.

In Fig. 1 are shown the relevant form factors according to (5) and (7) together with the structure factor for liquid N_2 as measured by Furumoto and Shaw.[14] Also shown is the sum of all a's neglecting incoherent scattering. Figure 1 shows that for $\kappa < 7$ Å^{-1} only the center-of-mass motion through $\tilde{S}_{\mathrm{coh}}(\kappa,\omega)$ and the rotational transition of $l = 2$ (the "d wave") play a significant role in the coherent scattering. It should be noted that $S_2(\omega)$ plays a central role in rotational Raman scattering as well as in NMR experiments. For small wave vectors, however, the incoherent scattering $a_{\mathrm{inc}}\tilde{S}_{\mathrm{inc}}(\kappa,\omega)$ may contribute significantly. The total coherent scattering using (3a) is $a_{\mathrm{coh}}S(\kappa)$, compared with a_{inc}, which according to (3b) measures the total incoherent scattering. Since $S(\kappa)$

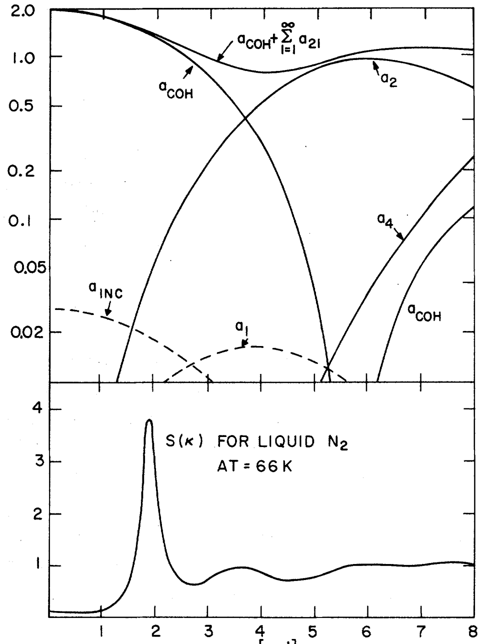

FIG. 1. Form factors of interest for the interpretation of the cross section for molecular nitrogen. The dashed lines correspond to an estimate of $\sigma_{\mathrm{inc}}/\sigma_{\mathrm{coh}}=0.03$, as discussed in the text. Also shown is the liquid structure factor, measured by Furumoto and Shaw.

~ 0.1 for the $\kappa < 1$ Å^{-1}, the two contributions are comparable, if one uses the finite value of $\sigma_{\mathrm{inc}}/\sigma_{\mathrm{coh}}$ given above.

Sears's theory provides an interesting possibility of comparing the motion of the molecular centers of N_2 to that of argon atoms. This was originally proposed by Vineyard[15] on the basis of the principle of corresponding states, which holds for a class of classical fluids having interaction potentials of the form

$$V(r)=\epsilon f(r/\sigma), \tag{8}$$

where the function $f(x)$ is characteristic of the class and r is the distance between two interacting elements of the fluid. ϵ and σ are the potential parameters of unit energy and length. ϵ, σ, and $\tau=\sigma(M/48\epsilon)^{1/2}$ are then used to define the reduced ("scaled") argument of the scattering $\kappa^*=\kappa\sigma$, $\omega^*=\omega\tau$. (Note our definition of τ, which is the one adopted by Levesque, Verlet, and Kürkijarvi.[19] Further, the particular state of the liquid under investigation is characterized by the reduced temperature $T^*=k_BT/\epsilon$ and density $\rho^*=\rho\sigma^3$. The principle of corresponding states then says that the reduced scattering law,

$$\tilde{S}^*_{\mathrm{coh}}(\kappa^*, \omega^*;\ T^*, \rho^*)=\tau\tilde{S}_{\mathrm{coh}}(\kappa, \omega;\ T, \rho), \tag{9}$$

depends only on the functional form of $f(x)$. The same result is obtained for S_{inc}. In Table I are shown the parameters ϵ, σ, τ for the molecular Lennard-Jones parameters for argon and nitrogen, together with the states where neutron scattering has been performed. Since the recent molecular-dynamics-simulation studies[3] of N_2 have been based on a diatomic potential, we also show the parameters of this potential.

TABLE I. Lennard-Jones potential parameters for the liquids Ar and N_2, shown together with the reduced temperatures and densities, where neutron-scattering (NS) and molecular-dynamics-simulation (MD) experiments have been performed. Note the definition $\tau=[M\sigma/(48\epsilon)]^{1/2}$. For nitrogen both the molecular (N_2) and the atomic (N) parameters are given. The bond length $d=1.094$ Å is also of importance in the atomic potential.

	σ (Å)	ϵ/k_B (K)	$\hbar/\tau$ (meV)	T^*_{NS}	ρ^*_{NS}	T^*_{MD}	ρ^*_{MD}
Ar	3.405	119.8	2.11	0.71	0.83	0.72	0.84
N_2	3.70	94.9	1.96	0.70	0.93	0.66	0.96
N	3.341	44.0	2.20	1.51	0.68	1.43	0.70

From Table I it is seen that our experiment on liquid N_2 is performed at T^* and ρ^* that correspond closely to the values for liquid Ar in the experiments of Sköld *et al.*,[10] and in Secs. V and VI we compare the results obtained through the scaling relation (9). It should, however, be noticed that Sears's theory is unable to explain finer details in the structure factor obtained both by x-ray[14] and neutron diffraction.[15] This seems to indicate that angular correlations are significant in liquid N_2, i.e., that the internal motions, characterized here by $S_l(\omega)$, cannot be strictly separated from the motions of the molecular centers. In our case, however, interpretation within Sears's approximate formalism seems reasonable. According to (5) and the discussion given above, (1) may then be analyzed in the following form:

$$S_{n,\mathrm{coh}}(\kappa, \omega)=a_{\mathrm{coh}}(\kappa)S_{\mathrm{coh}}(\kappa, \omega) + a_2(\kappa)\int_{-\infty}^{\infty}\tilde{S}_{\mathrm{inc}}(\kappa, \omega-\omega')S_2(\omega')\,d\omega', \tag{10a}$$

$$\tilde{S}_{n,\mathrm{inc}}(\kappa, \omega)=\tfrac{1}{2}a_{\mathrm{coh}}(\kappa)S_{\mathrm{inc}}(\kappa, \omega). \tag{10b}$$

From (10) and the values of the form factors shown in Fig. 1 it appears that for $1<\kappa<2.2$ Å^{-1}, $\tilde{S}_{\mathrm{coh}}(\kappa, \omega)$ is studied solely, whereas in the region $4.5<\kappa<6.5$ Å^{-1} information about $\tilde{S}_{\mathrm{inc}}(\kappa, \omega)$ and $S_2(\omega)$ is obtained.

III. EXPERIMENTAL

In order to measure $d^2\sigma/d\omega\,d\Omega$ in the regions of special interest as described in Sec. II, we per-

TABLE II. Scans performed in order to obtain the data. PG is pyrolytic graphite. When PG was used as monochromator, a PG filter was used to remove second order neutrons.

Wave-vector transfer κ (Å^{-1})	Energy transfer $\hbar\omega$ (meV)	Incident energy E_0 (meV)	Incident wave vector k_0 (Å^{-1})	Monochromator	Filter Crystal [*hkl*]	Analyzer	Energy resolution FWHM (meV)
0.1	$-1 \rightarrow 1$	15.39	2.727	Ge[311]	⋯	PG[004]	0.32
1.0, 1.3, 1.6, 1.9, 2.2	$-2 \rightarrow 2$	5.005	1.555	PG[002]	Be	PG[002]	0.17
1.9, 2.2, 4.0	$-10 \rightarrow 10$	14.60	2.656	PG[002]	PG	PG[002]	0.90
4.0, 4.8, 5.6, 6.4	$-18 \rightarrow 18$	41.92	4.5	Ge[111]	⋯	PG[002]	5.5

formed constant κ scans in the region $0.1 \leq \kappa \leq 6.4$ Å^{-1} on the Risø triple-axis spectrometer TAS III. In Table II are shown the scans together with the corresponding spectrometer characteristics. The energy resolution was determined from the elastic incoherent scattering of vanadium. Except for the $\kappa = 0.1$ Å^{-1} experiment (and to some extent at $\kappa = 2.2$ Å^{-1}), the incoming neutron energy E_0 was chosen so that the energy resolution was small enough so that no energy deconvolution was necessary. Having done this it was easily seen that the wave-vector resolution played no role. In some cases two experiments with different incoming energies were matched together to meet the requirements of high resolution at $\omega \sim 0$, as well as that of accessing large energy transfers. Any second-order contamination from the monochromator system was removed either by a pyrolytic graphite or a cooled beryllium crystal filter. For the experiment at $\kappa = 0.1$ Å^{-1} the determining factor was that the neutron velocity $\hbar k_0$ had to be greater than the sound velocity $v_S = 947$ m/sec of liquid N_2 at $T = 66.4$ K.[16] Then the monochromator, the analyzer, and the collimation were chosen in order to optimize the wave-vector and energy resolution, but in this case the measured spectra appear as an effective convolution of the cross section and the resolution function of the spectrometer.

The liquid N_2 was kept in a 15-mm-i.d. aluminum container and kept under saturated vapor pressure at $T = 66.4$ K within 0.1 K. The multiple scattering was calculated using Blech and Averbach's[17] results, $\sigma_{\text{coh}} = 11.1$ b, and an absorption cross section at wavelength 1.09 Å of 1.1 b. This gave the multiple scattering relative to the coherent one of 29%, taking the height of the scattering volume to be represented by the height of the neutron beam (40 mm).

IV. NEUTRON-SCATTERING RESULTS

Figure 2 shows typical neutron intensities obtained from the experiments listed in Table II. It is seen that except for the scans at $\kappa = 0.1$ Å^{-1}, the central part of the spectra could be measured with an energy resolution appreciably smaller than the observed width. However, since the distortion of the true line shape by the finite instrumental energy resolution depends on the functional line shapes of both the true spectrum and the resolution function, we cannot in general deduce the true width from the measured one. In order to estimate the error in the width, we assume a Gaussian line shape for the energy resolution (this is well verified), and a Lorentzian for the true spectrum (this seems to be a reasonable approximation in other

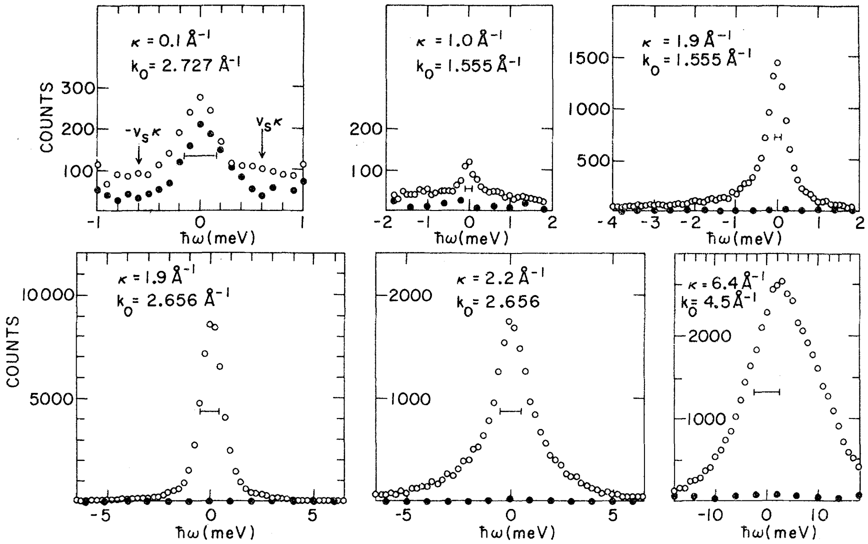

FIG. 2. Measured neutron intensities shown for some characteristic scans. Squares correspond to scattering from the empty can, and the horizontal bars show the energy resolution (FWHM).

liquids in this κ region), which gives an error of less than 10%, except for the spectrum at 2.2 Å^{-1}, where the error is 18%.

From the counting rates it appears that the intensities at smaller wave vectors are rather low when sufficient energy resolution is used. One consequence is that the smaller the wave vector, the less reliable become the data. On the other hand, it has been argued that the spectra for larger values of κ are independent of the liquid and therefore uninteresting to study. The experimental evidence now available, however, does not support

TABLE III. Symmetrized coherent scattering law $\tilde{S}_{n,\mathrm{coh}}(\kappa, \omega)$ for liquid nitrogen at 66.4 K at wave vectors $\kappa = 1.0$, 1.3, 1.6, 1.9, 2.2 Å^{-1}.

ħω (meV) \ κ (Å^{-1})	1.0	1.3	1.6	1.9	2.2
0.00	0.271	0.200	0.569	3.865	0.585
0.10	0.216	0.194	0.545	3.380	0.575
0.20	0.156	0.202	0.468	2.469	0.512
0.30	0.111	0.164	0.404	1.737	0.525
0.40	0.093	0.105	0.361	1.261	0.513
0.50	0.083	0.137	0.270	0.949	0.390
0.60	0.092	0.124	0.263	0.735	0.356
0.70	0.075	0.081	0.252	0.620	0.313
0.80	0.059	0.079	0.255	0.564	0.287
0.90	0.053	0.095	0.218	0.445	0.310
1.00	0.078	0.084	0.175	0.340	0.285
1.10	0.073	0.080	0.175	0.360	0.251
1.20	0.066	0.079	0.155	0.313	0.156
1.30	0.060	0.048	0.147	0.253	0.176
1.40	0.066	0.059	0.138	0.235	0.207
1.50	0.049	0.042	0.103	0.229	0.144
1.60	0.055	0.047	0.122	0.197	0.163
1.70	0.031	0.054	0.099	0.162	0.149
1.80	0.030	0.022	0.131	0.146	0.110
2.00				0.121	0.112
2.25				0.101	0.104
2.50				0.080	0.088
2.75				0.071	0.069
3.00				0.052	0.069
3.25				0.049	0.062
3.50				0.041	0.049
3.75				0.039	0.048
4.00				0.026	0.038
4.25				0.030	0.035
4.50				0.024	0.028
4.75				0.022	0.029
5.00				0.018	0.022
5.25				0.016	0.025
5.50				0.017	0.017
5.75				0.016	0.017
6.00				0.013	0.019
6.25				0.013	0.016
6.50				0.012	0.016
6.75				0.013	0.014
7.00				0.009	0.011
7.25				0.010	0.012
7.50				0.009	0.012
7.75				0.011	0.009
8.00				0.011	0.009
8.25				0.009	0.011
8.50				0.011	0.013
8.75				0.009	0.012
9.00				0.010	0.012

TABLE IV. Symmetrized coherent scattering law $\tilde{S}_{n,\mathrm{coh}}(\kappa,\omega)$ for liquid nitrogen at 66.4 K at wave vectors $\kappa=4.0$, 4.8, 5.6, 6.4 Å^{-1}.

$\hbar\omega$ (meV) \ κ (Å^{-1})	4.0	4.8	5.6	6.4	$\hbar\omega$ (meV) \ κ (Å^{-1})	4.0	4.8	5.6	6.4
0	0.121	0.051	0.066	0.056	8	0.021	0.022	0.028	0.028
1	0.103	0.051	0.064	0.055	9	0.016	0.018	0.024	0.025
2	0.079	0.048	0.060	0.054	10	0.0125	0.0151	0.0180	0.0210
3	0.068	0.044	0.055	0.048	11	0.0122	0.0111	0.0156	0.0182
4	0.049	0.041	0.050	0.045	12	0.0071	0.0095	0.0115	0.0145
5	0.038	0.035	0.044	0.041	13	0.0080	0.0080	0.0095	0.0120
6	0.026	0.030	0.037	0.036	14	0.0063	0.0064	0.0074	0.0087
7	0.023	0.026	0.033	0.032					

this viewpoint, and it would be useful if the theoretical results were evaluated in a more complete wave-vector and energy space. In our case the major problem at small wave vectors is the possible incoherent scattering contribution discussed in Sec. V B.

For $\kappa=0.1$ Å^{-1} the measured spectrum appears as a convolution of the scattering law and the resolution function of the instrument. This represents the ultimate limit of our possibility for doing neutron Brillouin scattering, i.e., by using neutrons of velocity higher than the sound velocity of the liquid, to scan through the Rayleigh-Brillouin triplet at low κ's. In this case both wave-vector and energy resolution are important and further, since the total scattering is very low, the intensity of the neutrons scattered from the sample at each point was only about 100 counts/h.

The spectra were corrected for the sensitivity of the spectrometer taking all changes of the analyzer system into account,[18] and normalized through the relation (3a) using the values for the structure factor $S(\kappa)$ shown in Fig. 1. In Tables III and IV are shown our results for the symmetrized scattering law $\tilde{S}_{n,\mathrm{coh}}(\kappa,\omega)$. Figure 3 shows the smoothed scattering law.

In Sec. V we interpret the observed scattering law according to the concepts introduced in Sec. II. In Sec. V A the inelastic small-angle scattering is discussed and in Secs. V B and V C we compare our results for $\tilde{S}_{\mathrm{coh}}(\kappa,\omega)$ and $\tilde{S}_{\mathrm{inc}}(\kappa,\omega)$, respectively, to the results for liquid Ar.

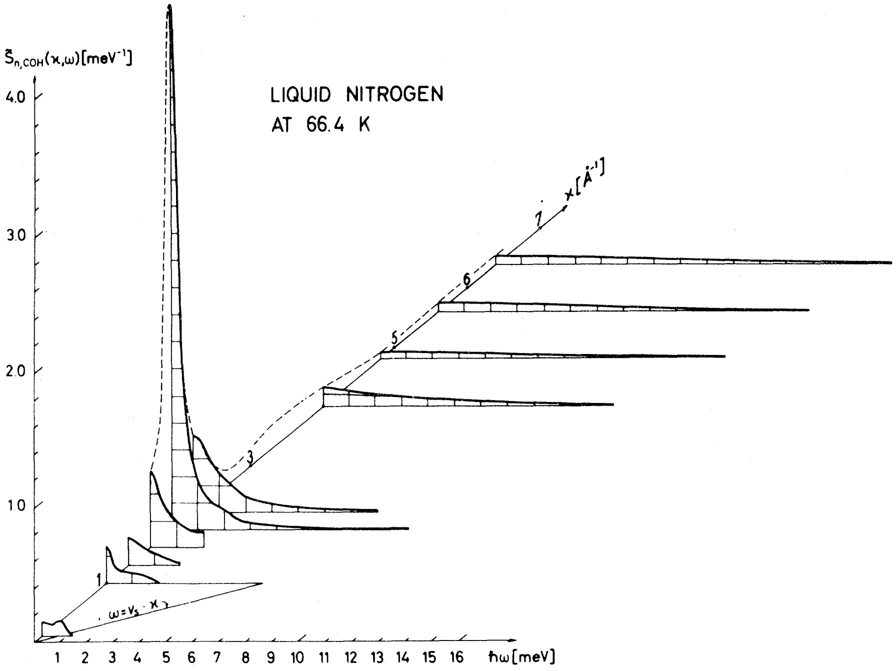

FIG. 3. Coherent scattering law for liquid N_2 at 66.4 K. At $\kappa=4.0$ Å^{-1} the scattering is separated according to the form factors shown in Fig. 1.

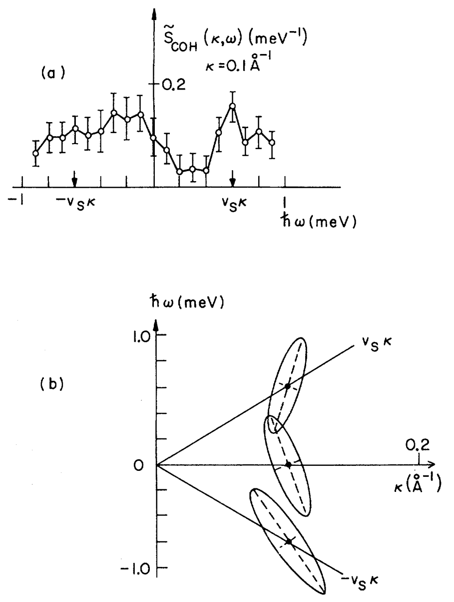

FIG. 4. (a) Observed coherent scattering law for the molecular centers of liquid N_2, distorted by the instrumental resolution; (b) resolution function, schematically shown to illustrate the distortion.

V. DISCUSSION

A. $\kappa=0.1$ Å^{-1}

In the computer simulation studies on Lennard-Jones fluids simulating liquid Ar, Levesque *et al.*[19] found a propagating mode at $\omega=v_S\kappa$ at $\kappa=0.2$ Å^{-1}, disappearing at $\kappa\sim2.5$ Å^{-1}, a feature that has not been searched for by neutron scattering. The existence of this Brillouin-like peak in the scattering law cannot be explained by simple hydrodynamical theory, but a coupling between transverse and longitudinal modes explained the simulated results well, and the authors related this particular feature to the existence of a long-time tail in the shear viscosity. Considering the intense interest in the subject of the tails in the correlation functions in dense fluids, we tried to look for the characteristic Brillouin-Rayleigh triplet in liquid N_2.

As mentioned above, the instrumental resolution plays an important role in this experiment, seriously distorting the real spectrum. We felt that the molecular-dynamics result at $\kappa=0.2$ Å^{-1} might be smeared out by instrumental resolution, so we decided to measure at $\kappa=0.1$ Å^{-1}. Figure 4(a) shows the result obtained for $\tilde{S}(\kappa,\omega)$ for liquid N_2 after the small sensitivity correction. It is seen that the observed spectrum is consistent with the existence of propagating sound modes, although these preliminary data suffer from large statistical uncertainties.

The asymmetric shape of $\tilde{S}_{\text{coh}}$ may be explained as a resolution effect. This is visualized in Fig. 4(b), where the half-width contours of the (κ,ω) resolution ellipse are shown for the three settings $\omega=0$ and $\omega=\pm v_S\kappa$ of the instrument, based on the theory of Møller and Nielsen.[20] Although the setting is nominally symmetric, the effective scattering does not contribute symmetrically, qualitatively explaining the shape in Fig. 4(a). Consequently, our experiments seem to be fully consistent with the computer simulation of Lennard-Jones fluids near the triple point. In liquid He, Ne, and Rb the extended sound mode has also been observed by neutron scattering. In the two former cases the low velocity of sound considerably facilitates the experiment, whereas in Rb the large intrinsic widths of the spectra made the instrumental distortion of the spectra negligible.

B. 1 Å$^{-1}<\kappa<2.2$ Å^{-1}

In the spectra obtained for wave vectors 1.0, 1.3, 1.6, 1.9, 2.2 Å^{-1}, no evidence is found for well-defined propagating collective density excitations in liquid N_2, since no inelastic peak is seen in $\tilde{S}_{n,\text{coh}}(\kappa,\omega)$ for constant values of κ. In this respect N_2 is qualitatively similar to Ar. Following Sears's theory, these spectra fall in the region where only scattering according to the form factor a_{coh} is of importance. However, as mentioned above, for $\kappa\lesssim1.5$ Å^{-1} both coherent and incoherent scattering may be of significance, as described by (10). Whereas the form for $S_{n,\text{coh}}$ is unknown, $S_{n,\text{inc}}$, by analogy to other liquids, is expected to be well approximated by the expression for simple diffusion,

$$\tilde{S}_{n,\text{inc}}=\frac{1}{\pi}\,\frac{D\kappa^2}{\omega^2+(D\kappa^2)^2}\,, \tag{11}$$

where D is the self-diffusion coefficient. Since for $\kappa=1.0$ and 1.3 Å^{-1} the observed spectra in a natural way separate into a narrow line and a broader one, one could suspect the narrow part to be incoherent scattering. Using the value for D discussed in Sec. V C and a value $\sigma_{\text{inc}}/\sigma_{\text{coh}}=0.03$ we can separate the observed scattering, but the narrow line does not disappear from the coherent spectrum, unless D is taken to be much larger than found by direct observation (see Sec. V C). We thus conclude that, independent of our interpretation within reasonable limits of $\sigma_{\text{inc}}/\sigma_{\text{coh}}$ and D, at least part of the narrow line in the observed spectra at $\kappa=1.0$ and 1.3 Å^{-1} is due to coherent scattering. At larger wave vectors the incoherent scattering can be neglected.

If we take the spectra listed in Table III to describe $\tilde{S}_{n,\text{coh}}(\kappa,\omega)$ for liquid N_2, $\tilde{S}^*_{\text{coh}}(\kappa^*,\omega^*)$ may

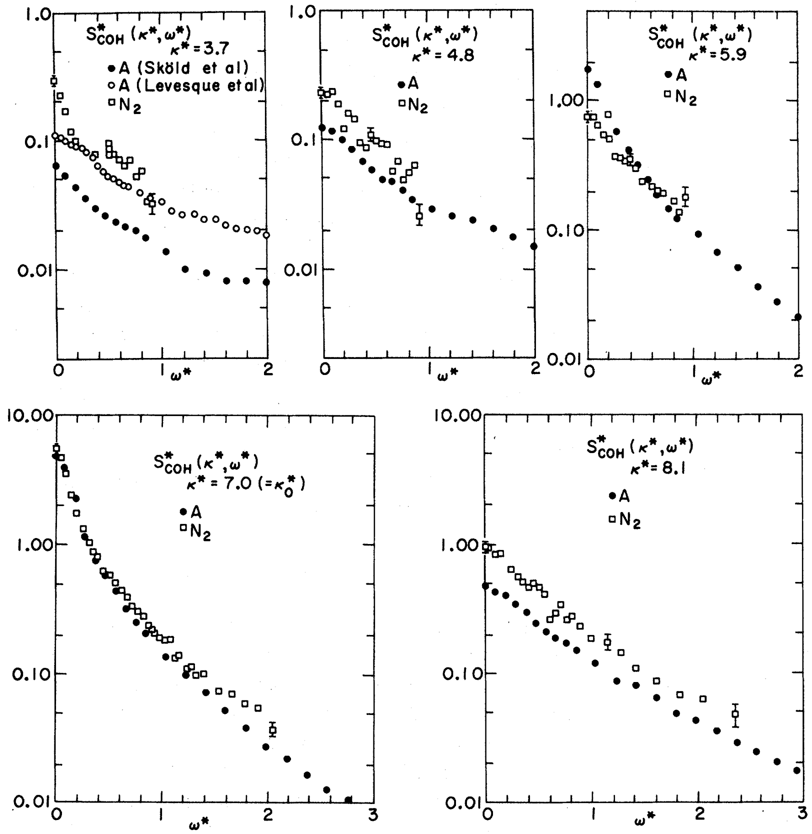

FIG. 5. Dimensionless coherent scattering law $S^*_{coh}(\kappa^*,\omega^*)$ for the molecular centers of liquid N_2 obtained from the theory of Sears, and compared to the same function for liquid Ar.

be deduced using (10a) and (9). In Fig. 5 is shown this function for the two liquids N_2 and Ar. The over-all agreement between the two liquids is a strong indication that the isotropic Lennard-Jones potential is appropriate concerning their dynamical behaviors. As pointed out by Sears, deviation from scaling according to (9) between N_2 and Ar may be taken as significant for anisotropic interactions in liquid N_2. Considering the preliminary nature of our data concerning multiple scattering (and consequently normalization), as well as the energy transfers covered, we cannot conclusively discuss this interesting subject. However, one feature seems to indicate that the anisotropic interactions influence the spectra. Particularly at $\kappa^*=3.7$ and 5.9, the agreement is poor for $\omega^* \lesssim 0.4$, and this may be compared to the rotational

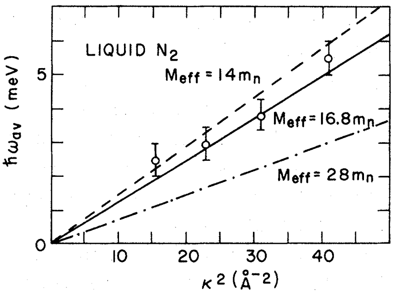

FIG. 6. Average energy of $S_{n,coh}(\kappa,\omega)$ for liquid N_2. The three lines correspond to the result of a Boltzmann gas with different effective masses, M_{eff}, as discussed in the text.

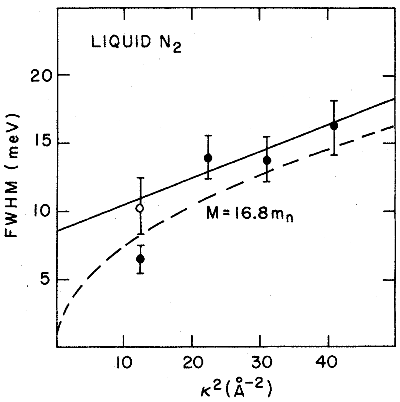

FIG. 7. Full width at half-maximum of $\tilde{S}_{n,coh}$ for liquid N_2. The dashed line corresponds to the result for a Boltzmann gas with $M_{eff}=16.8m_n$. The open circle is obtained after subtraction of the first term in (10a) and the straight line corresponds to the interpretation according to the theory of Sears.

frequency distribution, as deduced in Sec. VC. We find there that the distribution according to each angular momentum l has a half-width at half-maximum of $\omega_l = l(l+1)D_r$, where D_r is the rotational diffusion coefficient. Using the value found for D_r we get $\omega_l^* = 0.22 l(l+1)$, implying that the anisotropic interactions occur primarily within the $l=1$ state.

C. $4.0\ \text{Å}^{-1} \leqslant \kappa \leqslant 6.5\ \text{Å}^{-1}$

In this wave-vector region $S_{n,\mathrm{coh}}(\kappa, \omega)$ consists of broad inelastic lines. It is of interest to compare these lines to those characteristic for a noninteracting Boltzmann gas, according to which the lines should be Gaussians centered around the recoil energy $E_R = \frac{1}{2}(\hbar\kappa)^2/M_{\mathrm{eff}}$ and a width FWHM $= 2.36\hbar\kappa\ (k_B T/M_{\mathrm{eff}})^{1/2}$. The mass M_{eff} entering the scattering law is, however, not uniquely defined. The molecular mass is $28 m_n$, but in the ultimate limit of large κ, M_{eff} will be the nuclear one of $14 m_n$. However, since the frequencies involved in our experiment are very small compared to the vibrational ones, we expect the Sachs-Teller argument to be valid, giving $M_{\mathrm{eff}} = \frac{6}{5}(14 m_n) = 16.8 m_n$.[21] Further, since the line shapes do not appear to be Gaussian, we use for the center frequency the mean between the full width at half-maximum intersections with the line shape ω_{av}. In Figs. 6 and 7 we show ω_{av} of $S_{n,\mathrm{coh}}(\kappa, \omega)$ and the FWHM of $\tilde{S}_{n,\mathrm{coh}}(\kappa, \omega)$, respectively. It is seen that the agreement is fair.

Following Sears' theory the scattering at $4.0 \leqslant \kappa \leqslant 6.5\ \text{Å}^{-1}$ consists mainly of the last term in (10a). In this limit one must consider both $\tilde{S}_{\mathrm{inc}}$ and S_2, which considerably limits the information that can be gained about the two functions.

In order to analyze the data, we use simple models for the two scattering laws. We assume $\tilde{S}_{\mathrm{inc}}(\kappa, \omega)$ to be described by (11) and similarly the rotational motion to be simple rotational diffusion,

$$S_l(\omega) = \frac{1}{\pi} \frac{(l+1)D_r}{[l(l+1)D_r]^2 + \omega^2}, \tag{12}$$

when D_r is the rotational diffusion coefficient.[12] Inserting (11) and (12) into the last term of (10a) we get a Lorentzian line shape with full width W at half-maximum,

$$W = 12 D_r + 2 D \kappa^2. \tag{13}$$

Before using (13) we have to separate the spectrum at $\kappa = 4.0\ \text{Å}^{-1}$ according to the form factors in (10), since only the scattering according to $a_2(\kappa)$ should be used in (13). Having done this we obtain from (13) $D = 1.5 \times 10^{-5}$ cm²/sec for the self-diffusion coefficient and $D_r = 0.71 \times 10^{12}$ sec⁻¹.

TABLE V. Values for the self-diffusion coefficient D in liquid N_2 at 66.4 K, as observed by NMR, computer simulation (MD), and neutron scattering (NS). Also shown is the value obtained according to the concept of corresponding states, using the value from either MD or NS.

Technique	Reference	D (10^{-5} cm²/sec)
NMR	4	1.2
MD	3	1.2
NS	•••	1.5
Scaling	10	2.04

The value for D is in reasonable agreement with extrapolated values obtained from NMR experiments[4] and from computer simulation,[3] as shown in Table V. However, the value for D obtained[10] from corresponding states of Ar is significantly greater than the one observed, suggesting a contribution from anisotropic interaction in liquid N_2.

Considering our value for D_r, our assumption (12) for $S_l(\omega)$ is equivalent to assuming

$$F_l(t) = e^{-t/\tau_l}, \tag{14}$$

where $\tau_l = [l(l+1)D_r]^{-1}$. Hence we obtain $\tau_1 = 0.71$ psec and $\tau_2 = 0.24$ psec. The assumption of rotational diffusion is consistent if τ_l is small compared to the characteristic period of the rotation $T_{\mathrm{rot}} = 2\pi/\omega_{\mathrm{rot}}$, where $\omega_{\mathrm{rot}} = (k_B T/I)^{1/2}$ is the most probable frequency of a classical free rotator and I is the moment of inertia of the N_2 molecule. We get $\tau_l/T_{\mathrm{rot}} = 0.3$ and 0.1 for $l=1$ and 2, respectively, in favor of the assumptions leading to (13) and (14).

The value for D_r compares well with Sears's estimate at the boiling point of $D_r = 0.93 \times 10^{12}$ sec⁻¹, and our τ_2 is in close agreement with the NMR ex-

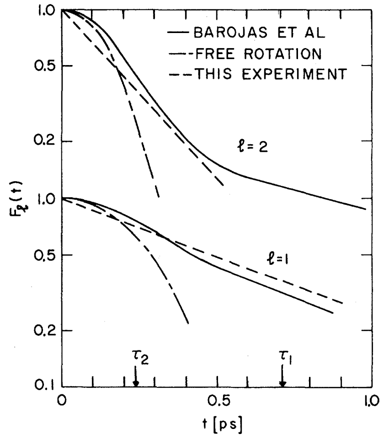

FIG. 8. Rotational relaxation functions $F_l(t)$ for liquid N_2, shown for $l=1$ and $l=2$. Solid line: computer simulation; dashed line: result of neutron scattering when rotational diffusion is assumed; dot-dash curve: result for the free rotator.

perimental value.[22] Further, in Fig. 8 we compare our $F_1(t)$ and $F_2(t)$ to the calculations in Ref. 3. Noting that, because of our simple treatment we cannot reproduce the finer structure of their results, we find the agreement satisfactory.

Consequently, on the basis of ω_{av} and the FWHM of $\tilde{S}_{n,\mathrm{coh}}$, we get good agreement with both the scattering from a noninteracting gas of classical free rotators and Sears's theory. However, taking into account the limited further information from the line shapes of the measured spectra, we point towards the latter as being more appropriate.

VI. CONCLUSIONS

We have performed neutron inelastic measurements on liquid N_2 at 66.4 K and saturated vapor pressure. Care was taken to minimize the instrumental resolution effects and multiple scattering, although the latter to some extent limits the conclusions that we can draw from the experiments.

At very small wave vectors, $\kappa = 0.1$ Å^{-1}, our data are consistent with the molecular dynamics simulations, showing that the sound modes seem to propagate at larger wave vectors than prescribed by linear hydrodynamic theory. Levesque *et al.*[19] took this for evidence of the coupling between transverse and longitudinal modes, and related it to the long-time tail in the velocity self-correlation functions. We feel that the strong interest in this and related problems of the decay of correlation functions justify more work along these lines.

At larger wave vectors, $\kappa \geq 1.0$ Å^{-1}, no evidence is found for propagating density modes in liquid N_2. By applying the theory of Sears we can separate the rotational motion from the motion of the molecular centers, which allows us to compare our result to those obtained from liquid Ar using scaling according to the principle of corresponding states. The coherent scattering law for the molecular centers in liquid N_2 scales well with the results for liquid Ar, but details disagree in a way that may be naturally related to translation-rotation (anisotropic) coupling. Only limited information can be obtained on the incoherent scattering, but the self-diffusion coefficient measured by our experiment agrees reasonably well with the values obtained by computer simulation and also by NMR experiments. However, these values are significantly lower than the values obtained when scaled from an isotropic Lennard-Jones liquid, which seem also to give evidence for the importance of anisotropic effects. The deviation from scaling between liquid N_2 and Ar is to some extent unexpected. Since the molecular ordering temperature is $T = 35.6$ K in the solid phase, one might not expect the short-range anisotropic interactions to be of great importance in the liquid phase above 64 K. Further, the small bond length $d = 1.094$ Å compared with $\sigma = 3.7$ Å makes the geometrical shape of the N_2 molecule rather isotropic. The experimental evidence mentioned above, together with the recent neutron-diffraction and molecular-dynamics results on the structure of liquid N_2, show, however, that the anisotropic part of the interaction potential cannot be neglected.

Finally, the information obtained from the rotational relaxation in liquid N_2 is in fair agreement with NMR experiments and computer simulation. We feel, however, that more accurate information might be gained and that more extensive measurements should be performed.

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